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(54) Title: METHOD FOR DELIVERING CHEMICALS TO AN OIL OR GAS WELL

(57) Abstract: A method of delivering chemicals to well such as an oil or gas well, the method comprising encapsulating the chemicals in or on a carrier particle such as starch, and delivering the carrier-encapsulated chemical to the well.

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WO 02/12674 A1

## METHOD FOR DELIVERING CHEMICALS TO AN OIL OR GAS WELL

1  
2  
3 This invention relates to a method for encapsulating  
4 chemicals and particularly to a method for starch  
5 and wax encapsulation of aggressive chemicals for  
6 applications in the oil industry. The invention  
7 relates especially to a method of delivering  
8 chemicals to an oil or gas well, in encapsulated  
9 form.

10  
11 Advances in drilling and completion technology have  
12 revolutionized new field development and the use of  
13 sub-sea wells with long tiebacks is now common. The  
14 low temperatures and long fluid transport times  
15 under sub-sea conditions often result in a wide  
16 variety of production chemistry related problems,  
17 including corrosion, scale, wax and asphaltene  
18 deposition, hydrate formation, bacterial growth and  
19 the transport of viscous fluids including emulsions.  
20 The control of these problems is usually achieved by  
21 continuous chemical injection at the sub-sea well  
22 head along separate, multiple injection lines.

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1 The installation of multiple chemical injection  
2 lines is extremely expensive both for subsea  
3 wellhead and continuous downhole injection,  
4 especially in deepwater environments.

5

6 A deployment method which allowed a reduction in the  
7 number of chemical injection lines required to  
8 deliver the cocktail of chemicals required at each  
9 wellhead would offer significant cost benefits.

10

11 The deployment of combined chemical treatment  
12 packages, for example scale and corrosion  
13 inhibitors, has been considered as one method of  
14 reducing the number of chemical injection lines.  
15 This has been achieved on a limited commercial basis  
16 by blending selected oilfield chemicals together to  
17 form a compatible mixture. However, the development  
18 of combined chemical packages is fraught with  
19 difficulties due to compatibility issues and is  
20 limited to a small range of products and product  
21 types. This limits the types of combined treatment  
22 available and depending upon the nature of the  
23 problem often still results in the use of several  
24 injection lines.

25

26 According to the present invention there is provided  
27 a method of delivering a chemical to an oil or gas  
28 well, the method comprising associating the chemical  
29 with a carrier, and delivering the chemical plus  
30 carrier to the well.

31

1 The chemical can be encapsulated by the carrier or  
2 otherwise entrapped by the carrier. The carrier  
3 preferably comprises a suspension or slurry of  
4 particles onto or into which the chemical can be  
5 loaded. A typical carrier is particulate starch,  
6 but other good carriers can be encapsulating agents  
7 conventionally known from e.g. the food, paint and  
8 pharmaceutical industries, such as gum arabic,  
9 waxes, PVOH, polylactic acids, dextrans, low  
10 viscosity modified starches, arabinogalactan, gum  
11 acacia, casein, gelatin, carboxymethylcellulose,  
12 tragacanth, karaya, sodium alginate, tannin, and  
13 celluloses.

14  
15 We have found that deploying the chemicals on or in  
16 a slurry of nano/micro particles can alleviate  
17 compatibility issues during storage and deployment  
18 and thus facilitate the injection of multiple  
19 chemicals via a single chemical injection line. The  
20 nano/micro particles can typically contain a high  
21 active level of oilfield chemical, typically 5-  
22 90%v/v, and can be dispersed in either an aqueous or  
23 oleic medium, and in solution or suspension,  
24 depending upon the nature of the encapsulation  
25 matrix. The entrapped oilfield chemicals are  
26 typically released upon contact with the produced  
27 fluids due to the breakdown of the coating or  
28 carrier matrix either thermally and/or as a result  
29 of mixing with oil or water. The potential to  
30 control the rate and extent of release as a function  
31 of time can also allow chemicals to be transported  
32 and released along different sections of the

1 pipeline, thus alleviating some of the kinetic  
2 problems associated with scale, wax and hydrate  
3 inhibitors in long subsea tie backs.

4  
5 This can enable the simultaneous delivery of  
6 combined oilfield chemical packages to platform,  
7 remote and complex wells through a single injection  
8 line. The oilfield production chemical-entrapped  
9 particles could be injected topsides, at sub sea  
10 wellheads or elsewhere in the well. The particles  
11 could also be applied to deliver oilfield chemicals  
12 that cannot be effectively deployed by conventional  
13 solvents. Certain embodiments may include the  
14 delivery of a single oilfield chemical to a well  
15 while associated with a carrier such as the above-  
16 mentioned compounds.

17  
18 The chemical is typically injected continuously into  
19 the well, typically through a dedicated fluid line.

20  
21 The nano/micro particle entrapment technology can be  
22 applied to deliver a wide range and a wide  
23 combination of oilfield production chemicals down  
24 one injection line or umbilical. This includes, but  
25 is not limited to scale inhibitors, corrosion  
26 inhibitors, wax inhibitors, asphaltene inhibitors,  
27 hydrate inhibitors, oxygen scavengers, hydrogen  
28 sulphide scavengers, demulsifiers, biocides, gel  
29 breakers, tracers, friction reducers, surfactants,  
30 de-oilers and antifoaming agents. The oilfield  
31 chemicals can be entrapped in either liquid or solid  
32 form.

1 The particles can be manufactured using a variety of  
2 techniques including complex coacervation,  
3 interfacial polymerisation, desolvation, extrusion,  
4 agglomeration, emulsion polymerisation, gelation,  
5 chemical vapour deposition, fluid bed coating, spray  
6 drying and combinations thereof. The particles can  
7 be produced over a variable particle size,  
8 typically, 1nm-850 $\mu$ m and can contain a high active  
9 level of oilfield chemical, typically 1-90%v/v.  
10 Nano/micro particles containing different oilfield  
11 production chemicals can be dispersed into either an  
12 aqueous or oleic carrier fluid, that may or may not  
13 contain other oilfield production chemicals, using  
14 either ionic or non-ionic surface active agents.  
15 The material is preferably stable under injection  
16 conditions in both aqueous and non-aqueous  
17 environments at the ambient and sub-ambient  
18 temperatures that may be encountered in a production  
19 environment. The entrapped oilfield chemical can be  
20 rapidly released from the encapsulating and/or  
21 carrier medium as a result of either thermal  
22 degradation of the matrix and/or dissolution in  
23 either the oil or water phase, releasing the  
24 oilfield chemical under wellhead conditions. The  
25 release time of the chemical upon contact with the  
26 produced fluids could also be delayed depending upon  
27 the nature of the entrapment matrix. This can  
28 allow chemicals to be transported and released along  
29 different sections of the pipeline, thus enabling  
30 the release of chemicals in the right place and  
31 alleviating some of the kinetic problems associated

1 with scale, wax and hydrate inhibitors in long sub  
2 sea tie backs.

3

4 The entrapment of certain oilfield chemicals could  
5 reduce the corrosivity of the fluid to be deployed  
6 into the wellhead or downhole injection system.

7 This could permit the umbilicals and downhole  
8 injection lines to be fabricated from lower cost  
9 carbon steels rather than the more expensive  
10 stainless steels and/or corrosion resistant alloys.

11

12 The particles containing different production  
13 chemicals, in either solid or liquid form, can then  
14 be mixed together to produce the required blend of  
15 oilfield chemicals for dispersion into the fluid  
16 carrying medium which may be aqueous or organic  
17 based. The solid particles could be dispersed into  
18 the fluid-carrying medium by use of a wide range of  
19 different types of amphoteric, anionic, cationic and  
20 nonionic surface-active agents. Amphoteric  
21 surfactants could include acetates such as lauro-,  
22 alkyl- and coco-amphoacetates, betaines such as  
23 lauryl-, alkyl- and coco-amidopropylbetaines,  
24 glycines, imidazolines and propionates such as  
25 lauro-, alkyl- and coco-aminodipropionate. Anionic  
26 surfactants could include alkyl- alkylaryl-,  
27 alkylether and alkylarylether sulphonates and  
28 carbonates, lignin derivatives, olefine and paraffin  
29 sulphonates, phosphate esters and sarcosinates.  
30 Cationic surfactants could include amides, amines,  
31 amidoamines, diamines and quaternaries such as  
32 didecyldimethylammonium. Nonionic surfactants could



1 include alkoxylates such as alcohol-, alkylphenol-,  
2 amide-, ester-, fatty acid- and glyceride  
3 ethoxylates, alkylamides, amine oxides and esters.

4  
5 The required dispersing characteristics could be  
6 achieved for example by varying the ratio of a  
7 sorbitan ester and a sorbitan ester ethoxylate to  
8 achieve the desired hydrophilic - lipophilic balance  
9 (HLB).

10  
11 The chemical is typically coated or otherwise  
12 associated with a carrier such as starch, flour or  
13 wax. The starch can decompose at a given  
14 temperature releasing the chemical at a second  
15 location where it is needed. Selection of the  
16 characteristics of the carrier (e.g. starch) used  
17 allows accurate control over the temperature of  
18 decomposition. Normally the temperature at the  
19 wellhead will be hotter than the surface of the  
20 well. The precise temperature at the wellhead will  
21 vary from well to well, and typical subsea wellheads  
22 may have an ambient temperature of around 110°C  
23 (compared with 20°C at surface). The starch or wax  
24 coat can typically be designed to decompose when it  
25 crosses a point on the temperature gradient and so  
26 release the chemicals. In particular, wax carriers  
27 can be designed to degrade or dissolve slowly or  
28 after a set time has elapsed to release the  
29 chemicals continuously over a period of time or  
30 after a set interval e.g. in the production fluids.  
31 The starch or wax may be modified to decompose at  
32 different temperatures as may be necessary for



1 particularly shallow or particularly deep wells or  
2 for any other reason in which the temperature of the  
3 wellhead may be different from normal. The starch  
4 is typically granular starch, and resistant starch  
5 made therefrom. The chemical is typically adsorbed  
6 onto the starch, typically by simple mixing.  
7 Adjuncts useful in controlled release formulations  
8 can be added.

9  
10 All granular starches and flours (hereinafter  
11 "starch") may be suitable for use herein and may be  
12 derived from any native source. A native starch as  
13 used herein, is one as it is found in nature. Also  
14 suitable are starches derived from a plant obtained  
15 by standard breeding techniques including  
16 crossbreeding, translocation, inversion,  
17 transformation or any other method of gene or  
18 chromosome engineering to include variations  
19 thereof. In addition, starch derived from a plant  
20 grown from artificial mutations and variations of  
21 the above genetic composition, which may be produced  
22 by known standard methods of mutation breeding, are  
23 also suitable herein.

24  
25 Typical sources for the starches are cereals,  
26 tubers, roots, legumes and fruits. The native  
27 source can be corn, pea, potato, sweet potato,  
28 banana, barley, wheat, rice, sago, amaranth,  
29 tapioca, arrowroot, canna, sorghum, and waxy or high  
30 amylose varieties thereof. As used herein, the term  
31 "waxy" is intended to include a starch containing at  
32 least about 95% by weight amylopectin and the term

1 "high amylose" is intended to include a starch  
2 containing at least about 40% by weight amylose.

3  
4 Conversion products which retain their granular  
5 structure may be derived from any of the starches,  
6 including fluidity or thin-boiling starches prepared  
7 by oxidation, enzyme conversion, acid hydrolysis,  
8 heat and or acid dextrinization, and or sheared  
9 products may also be useful herein.

10  
11 Particularly useful are granular structures, which  
12 have been "pitted" by the action of enzymes or acid,  
13 leaving a still organised structure that creates a  
14 microporous starch. The enzymatic or acid hydrolysis  
15 of the starch granule is carried out using techniques  
16 well known in the art. The amount of enzyme used is  
17 dependent upon the enzyme, i.e., type, source and  
18 activity, as well as enzyme concentration, substrate  
19 concentration, pH, temperature, the presence or  
20 absence of inhibitors, and the degree and type of  
21 modification. Types of modifications are described  
22 herein, *infra*. These parameters may be adjusted to  
23 optimise the nature and extent of the "pitting" of  
24 the starch granule.

25  
26 Another particulate starch useful in the controlled  
27 release applications of the present invention is  
28 resistant starch. Resistant starch is commonly  
29 known as a starch not likely to be adsorbed in the  
30 small intestine of a healthy individual. Granular  
31 or particulate starches, such as of the RS2-type (a  
32 starch granule that resists digestion by pancreatic

1     alpha-amylase) and the RS4-type (a chemically  
2     modified starch, such as acetylated,  
3     hydroxyalkylated, or cross-linked starch) are  
4     particularly suitable. However, resistant starches  
5     of the RS3-type (retrograded, non-granular starch  
6     formed by heat/moisture treatment of starch) are  
7     also suitable for the instant invention due to their  
8     high level of retrogradation or crystallisation from  
9     the alignment and association of associated amylose.

10

11    These types of resistant starch are well known in  
12    the art and may be exemplified by that disclosed in  
13    US Patent Nos. US 5,593,503 which describes a method  
14    of making a granular resistant starch; US Patent  
15    Nos. 5,281,276 and 5,409,542 which describe methods  
16    of making resistant starches of the RS3 type; US  
17    5,855,946 which describes a method of making a  
18    resistant starch of the RS4-type; and U.S.  
19    Application Serial No. 60/157370, which describes  
20    the formation of a very highly resistant starch.  
21    The methods for making the resistant starches are  
22    described in the preceding references, the  
23    disclosures of which are incorporated herein by  
24    reference.

25

26    The starch particulate, including granular and  
27    resistant starches, may be modified by treatment  
28    with any reagent or combination of reagents that  
29    contribute to the controlled release properties of  
30    the starch.

31

1 Chemical modifications are intended to include  
2 crosslinked starches, including crosslinking the  
3 particulate starch with reactive polymers.  
4 Preferred reactive polymers include starches  
5 modified with aldehyde or silanol groups. Other  
6 chemical modifications include, without limit,  
7 acetylated and organically esterified starches,  
8 hydroxyethylated and hydroxypropylated starches,  
9 phosphorylated and inorganically esterified  
10 starches, cationic, anionic, non-ionic, and  
11 zwitterionic starches, and succinate and substituted  
12 succinate derivatives of starch.

13

14 Preferred modified starches are starch acetates  
15 having a degree of substitution ("DS") of about up  
16 to about 1.5, particularly those disclosed in US  
17 5,321,132, thereby improving compatibility with  
18 synthetic hydrophobic materials. Such  
19 modifications are known in the art, for example in  
20 Modified Starches: Properties and Uses, Ed.  
21 Wurzburg, CRC Press, Inc., Florida (1986).

22

23 Other suitable modifications and methods for  
24 producing particulate starches are known in the art  
25 and disclosed in U.S. Patent No. 4,626,288 which is  
26 incorporated herein by reference. In a particularly  
27 useful embodiment, the starch is derivatized by  
28 reaction with an alkenyl cyclic dicarboxylic acid  
29 anhydride by the method disclosed in U.S. Patent  
30 Nos. 2,613,206 and 2,661,349, incorporated herein by  
31 reference, or propylene oxide, more particularly by  
32 reaction with octenylsuccinic anhydride.

1 The encapsulated chemicals can be carried in a  
2 liquid-phase inhibitor or other chemical to be  
3 delivered to the well that may be incompatible with  
4 the encapsulated chemical. All chemicals to be  
5 delivered could then be injected through a single  
6 umbilical. Two umbilicals could be installed to  
7 allow operations to continue in the event of one  
8 blocking up. Additionally a third umbilical for  
9 methanol could be provided. A total of three  
10 umbilicals could therefore provide adequate cover  
11 for a well. This represents a significant saving  
12 when compared with the prior art, which requires  
13 five or six umbilicals for comparable performance.

14

15 Embodiments of the present invention will now be  
16 described by way of example with reference to the  
17 following examples.

18

19 **Example 1: Encapsulation of solid material**

20 US Patent 4755397 to Eden et al (incorporated herein  
21 by reference) describes a process for the starch  
22 encapsulation of a solid material, namely, ferric  
23 hydroxide, which can be adapted for the  
24 encapsulation of oilfield chemicals as follows.

25

26 The desired oilfield chemical is dissolved in  
27 acidified water, dilute sodium hydroxide is added as  
28 necessary while stirring to remove from the chemical  
29 any trace precipitates. Ammonium sulphate, water and  
30 high amylose (70%) cornstarch is added to the  
31 chemical slurry to give a slurry of the following  
32 composition:

1	Starch	410 grams	(19.9%)
2	Ammonium sulphate	610 grams	(29.6%)
3	Chemical	41 grams	(2.0%)
4	Water	1000 grams	(48.5%)

5 This slurry is processed through a jet cooker (Model  
6 C-1, National Starch & Chemical Corp) at 150°C. At  
7 this temperature the high amylose starch cooks,  
8 despite the presence of a high level of an  
9 inhibiting salt, and forms a uniform dispersion. A  
10 ball valve attached to the outlet of the jet cooker  
11 can be adjusted so that a pressure drop from maximum  
12 cooking temperature and pressure to atmospheric  
13 pressure occurs as the starch cook passes through  
14 the valve. Upstream the pressure is typically  
15 90psig; downstream the pressure is typically 0psig.  
16

17 As the starch passes through the valve and the  
18 pressure is reduced to atmospheric, its temperature  
19 drops to around 104°C, the boiling point of the salt  
20 solution at atmospheric pressure. At this  
21 temperature, the starch precipitates essentially  
22 instantaneously entrapping the solid oilfield  
23 chemical. The product collected at the cooker  
24 outlet is typically a slurry of tan particles 5 to 7  
25 microns in diameter. The slurry, by volume, is a  
26 third salt solution and two thirds precipitated  
27 particles. This product is washed free of salt and  
28 dried.  
29

30 The dried particles (40% by weight) containing the  
31 various oilfield chemicals are then mixed with a  
32 synthetic white oil such as Isopar M (52% by weight)

1 and a polyalkoxylated alkyl phenol based dispersant  
2 (5% by weight) using a high shear, UltraTurrax mixer  
3 at 5000 rpm for 10 minutes. A clay based thickening  
4 agent (3% by weight) is then added to this mix and  
5 blended using a high shear, UltraTurrax mixer at  
6 10,000 rpm.

7  
8 This process can be used for the production of  
9 encapsulated particles containing a) solid biocides;  
10 b) de-oilers; c) demulsifiers; d) scale inhibitors;  
11 e) corrosion inhibitors; f) wax inhibitors; and  
12 g) asphaltene inhibitors. The chemical-loaded  
13 particles are mixed in various combinations of  
14 chemicals and delivered through a single fluid  
15 delivery pipeline to a wellhead, where the  
16 temperature of around 110°C breaks down the starch  
17 particles and releases the chemicals. Optionally a  
18 liquid chemical such as a corrosion inhibitor is  
19 mixed with the carrier fluid conveying the particles  
20 to the well.

21  
22 **Example 2: Encapsulation of an Active Ingredient**  
23 WO9901214 to Fester et al (incorporated herein by  
24 reference) describes a process for the encapsulation  
25 of an active ingredient, namely, solids and water-  
26 soluble fluids. This can be adapted for  
27 encapsulation of oilfield chemicals as follows.

28  
29 Fifteen grams of PN (native potato starch) are added  
30 to 100ml water in which 2.5 g Tween 80 is dissolved.  
31 Four grams TSTP are dissolved in this suspension,  
32 followed by the addition of 20 g of salad oil. An



1 emulsion forms with the aid of an Ultra-Turrax.  
2 The o/w emulsion is then emulsified in a second  
3 hydrophobic phase, namely 200ml of paraffin oil. A  
4 top stirrer at a speed of 600 rpm is used for this  
5 purpose.

6  
7 A solution of 0.65g NaOH in 10ml water is  
8 subsequently added to the emulsion with stirring, in  
9 order to initiate partial gelation and cross-  
10 linking. After 30 minutes, the stirrer speed is  
11 increased to 1000 rpm. After 4 hours the emulsion is  
12 broken by addition of acetic acid.

13  
14 The starch particles collected in the water/acetic  
15 acid phase. After separation, the particles are  
16 washed with de-ionised water and stored.  
17 Examination of the dispersed fluid by light  
18 microscopy should indicate that the particles are  
19 essentially mono dispersed with a size of 25  $\mu\text{m}$   
20 containing droplets of oil.

21  
22 This process can be used for the production of  
23 encapsulated particles containing solid and/or  
24 liquid chemicals, namely, scale and corrosion  
25 inhibitors, oxygen and hydrogen sulphide scavengers,  
26 demulsifiers, gel breakers, tracers and antifoaming  
27 agents. However, the process could be applicable to  
28 any solid or water-soluble chemicals. As before the  
29 particulate- entrapped chemicals are mixed in  
30 various combinations of chemicals and delivered  
31 through a single fluid delivery pipeline to a  
32 wellhead, where the temperature of around 110°C

1 breaks down the starch particles and releases the  
2 chemicals. Again the liquid phase of the carrier  
3 fluid can incorporate a further chemical to be  
4 delivered to the well.  
5

6 **Example 3: Encapsulation of a Water Insoluble Liquid**

7 US Patent 4755397 to Eden et al (incorporated herein  
8 by reference) describes a process for the starch  
9 encapsulation of a water insoluble liquid, namely,  
10 peppermint oil, and this can be adapted for the  
11 production of starch encapsulation of hydrophobic  
12 oilfield chemicals as follows.  
13

14 A slurry is made of the following composition:

15	High Amylose (70%Corn Starch)	20%
16	Ammonium Sulphate	40%
17	Water	40%

18

19 The following is mixed, to disperse the hydrophobic  
20 oilfield chemical and added, with mixing, to the  
21 previous slurry:  
22

23	Oilfield chemical	2-10%
24	Surfactants	90-98%

25

26 The resulting slurry/coarse emulsion is jet-cooked  
27 through a C-1 cooker as in Example 1. In this case,  
28 the cooker outlet hose empties below the surface of  
29 a slurry of ammonium sulphate and ice in saturated  
30 ammonium sulphate solution (-8°C.) to condense and  
31 trap any free peppermint oil vapours. The resulting  
32 product is typically coarse (<20 mesh) light tan

1 powder in salt solution. The powder is recovered by  
2 filtration and dried.

3

4 A 3% weight aqueous solution of HEC is then prepared  
5 by slowly adding the powdered HEC to distilled water  
6 and gradually increasing the mixing speed over a  
7 five-minute period. Once a solution is formed a  
8 sorbitan ester ethoxylate based dispersant (6% by  
9 weight) is added to the aqueous HEC mixture and  
10 blended at 2000rpm for five minutes. The dried  
11 particles (50% by weight) containing the various  
12 oilfield chemicals are then mixed with the aqueous  
13 solution of HEC and dispersant using a high shear,  
14 UltraTurrax mixer at 5000 rpm for 10 minutes.

15

16 This process is particularly useful for  
17 manufacturing encapsulated products containing oil  
18 soluble scale and corrosion inhibitors, wax and  
19 asphaltene inhibitors, drag reducers, demulsifiers  
20 and de-oilers. A variety of these chemicals can be  
21 encapsulated as described above and delivered to a  
22 wellhead via a single injection line in various  
23 combinations, without interaction between the  
24 chemicals in the line during delivery. Upon arrival  
25 at the wellhead the starch capsules surrounding the  
26 chemicals are broken down by the ambient temperature  
27 at the wellhead, and the chemicals are released and  
28 activated in situ. Incorporation of incompatible  
29 liquid phase chemicals in the carrier fluid does not  
30 affect the encapsulated chemical.

31

1     **Example 4: Encapsulation of a solid or oil soluble**  
2     **product.**

3     US Patent 4997659 to Yatka et al (incorporated  
4     herein by reference) describes a process for the  
5     encapsulation of a powdered sweetener, namely,  
6     Alitame in paraffin and/or microcrystalline wax.  
7     This was adapted for the encapsulation of various  
8     solid oilfield chemicals as listed above.

9  
10    A 20% paraffin or micro-crystalline wax, of defined  
11    melting point/80% solid oilfield chemical is  
12    prepared by mixing the molten wax with the solid  
13    chemical, cooling to form an agglomerate and  
14    grinding up the agglomerate to form granules. These  
15    granules are optionally further processed to form  
16    spheres, using a spheroniser. The size of the  
17    spheres is controlled by the granulation process but  
18    is typically 1-50 $\mu$ m in diameter.

19  
20    This process is typically used to produce paraffin  
21    or microcrystalline wax-based particles containing  
22    solid oilfield production chemicals such as scale,  
23    wax and corrosion inhibitors, biocides and other  
24    scavengers. In addition the wax particles can be  
25    manufactured to entrap oil-based liquids such as  
26    corrosion, wax and asphaltene inhibitors,  
27    demulsifiers and de-oilers.

28  
29    The nano/micro particles containing different  
30    production chemicals, in either solid or liquid  
31    form, are dispersed together to produce the required  
32    blend of oilfield chemicals for dispersion into the

1 fluid carrying medium which was either aqueous or  
2 organic based. The solid particles are dispersed  
3 into the fluid-carrying medium by use of a wide  
4 range of different dispersants. Suitable  
5 dispersants include fatty acid esters and  
6 alkoxyated (e.g. methoxylated or ethoxylated) fatty  
7 acid esters such as sorbitan ester and sorbitan  
8 ester ethoxylate; and PEG esters such as PEG  
9 laurate. By varying the ratio of the ethoxylated  
10 sorbitan ester to the sorbitan ester the desired HLB  
11 can be obtained.

12

13 The encapsulated oil field chemicals are mixed in  
14 the desired proportions and delivered via a single  
15 fluid delivery line to a wellhead, at which point  
16 the wax capsules degrade, releasing the chemical  
17 into the wellhead environment. Optionally the two  
18 or more chemicals that are delivered to the well can  
19 be encapsulated by different methods e.g. according  
20 to any of the examples herein, so that the different  
21 particles release their chemical burdens at  
22 different points in the well, in response to  
23 different stimuli.

24

25 **Example 5: Encapsulation of a wax inhibitor by**  
26 **starch.**

27 A granular starch (150g, starch octenylsuccinate,  
28 aluminum salt, commercially available from National  
29 Starch and Chemical Company) was added to a wax  
30 inhibitor XPC 3147C (50 g, Aldrich) which had been  
31 melted at a temperature greater than 30°C. The  
32 mixture was stirred at ambient temperature and

1 pressure in a high shear disperser (Torrence,  
2 #785049) at 2000-4000 rpm. An additional 100 g of  
3 the granular starch was added to the mixture and  
4 stirred for two more minutes to form a fine, free-  
5 flowing powder. This is conveyed to a wellhead as  
6 previously described through a single fluid line by  
7 a carrier fluid that incorporates a scale inhibitor  
8 that is incompatible with the wax inhibitor, without  
9 any reaction between the chemicals. The scale  
10 inhibitor treats the fluid conduit continuously from  
11 the point of entry to the wellhead, and the wax  
12 inhibitor is activated only after a longer period of  
13 time as a result of the starch encapsulating matrix  
14 dissolving in the produced fluids.

15

16 **Example 6: Encapsulation of a water-soluble chemical**  
17 **by starch.**

18 Water-soluble solids were formulated with starch at  
19 a 1:1 ratio (50% loading on starch). The oil well  
20 chemical was solubilised in ambient water and  
21 homogenised for 1-2 minutes at 9000-10000 rpm  
22 (Silverson L4RT). The starch was then added to the  
23 solution and the mixture was further homogenised for  
24 2-3 minutes at 9000-10000rpm, 20°C (Silverson L4RT).  
25 The mixture was spray dried (40% solids, 375°F inlet  
26 temperature, 225°F outlet temperature with a feed  
27 rate of 160ml/minutes and dual wheel atomisation  
28 using Bowen Lab Model (30" x 36") to produce a  
29 flowable, non-sticky composition.

30

31 a. The example was carried out using a scale  
32 inhibitor, Scaletreat 2001-28, as the oil well

- 1 chemical and Vulca 90, a maize starch  
2 crosslinked with 1.5% epichlorohydrin on dry  
3 starch.
- 4 b. The example was carried out using a corrosion  
5 inhibitor, Corrtreat 2001-29 as the oil well  
6 chemical and a starch acetate (1.5 DS) waxy  
7 maize starch.
- 8 c. The example was carried out using a scale  
9 inhibitor, Scaletreat 2001-26 as the oil well  
10 chemical and a microporous waxy maize starch  
11 that was digested using 0.3% glucoamylase on  
12 dry starch to achieve 15% digestion.

13  
14 In each case, the encapsulated chemicals are mixed  
15 as desired and delivered in mixtures of encapsulated  
16 particles to the well-head through a single fluid  
17 line. The encapsulated particles are degraded by  
18 the fluid conditions at the well-head, and/or by  
19 temperature, thereby delivering their active  
20 reagents at the required position in the wellhead.

21  
22 **Example 7: Encapsulation of a water insoluble**  
23 **chemical by starch.**

24 Water insoluble solids were formulated with starch  
25 at a 1:1 ratio (50% loading on starch). The oil  
26 well chemical was added to a waxy maize starch  
27 modified with 3% octenyl succinic anhydride and  
28 converted to a water fluidity of 40, and the mixture  
29 was homogenised for 1-2 minutes at 9000-10000 rpm,  
30 20°C (Silverson L4RT). Water was added to the  
31 emulsion and the mixture was further homogenised, 1  
32 minute at 9000-10000 rpm, 20°C (Silverson L4RT).



1 The starch was then added to the solution and the  
2 mixture was further homogenised, 1-2 minutes at  
3 9000-10000 rpm, 20°C (Silverson L4RT). The mixture  
4 was spray dried (35% solids, 380°F inlet  
5 temperature, 230°F outlet temperature, 140-  
6 160ml/minutes with dual wheel atomisation using  
7 Bowen Lab Model (30" x 36")) to produce a flowable,  
8 non-sticky composition.

- 9
- 10 a. The example was carried out using a wax  
11 inhibitor, Waxtreat 398 as the oil well chemical  
12 and a microporous waxy maize which was 30%  
13 digested with 0.3% glucoamylase, and modified  
14 with 3% octenyl succinic anhydride and  
15 crosslinked with 1% aluminium sulphate.
- 16 b. The example was carried out using an asphaltene  
17 dispersant, Waxtreat 7302 as the oil well  
18 chemical and a microporous waxy maize starch  
19 modified using 3% octenyl succinic anhydride,  
20 enzymatically treated using 0.3% glucoamylase, to  
21 achieve 30% digestion.
- 22 c. The example was carried out using a hydrogen  
23 sulphide scavenger, Scavtreat 1020 as the oil  
24 well chemical and a high amylose corn starch,  
25 HYLON® VII starch, commercially available from  
26 National Starch and Chemical Company.
- 27 d. The example was carried out using a kinetic  
28 hydrate inhibitor, Hytreat 569 as the oil well  
29 chemical and a microporous (30% enzyme digested)  
30 waxy maize starch modified using 3% octenyl  
31 succinic anhydride, enzymatically treated using  
32 0.3% glucoamylase.

1 e. The example was carried out using an anti-  
2 agglomerate hydrate inhibitor, Hytreat A560 as  
3 the oil well chemical and a cationic starch  
4 silanol, 0.3% Nitrogen, 0.4% silanol.

5  
6 Chemicals are delivered through a single delivery  
7 line to a wellhead and also to a well bore and  
8 formation. The wellhead chemicals are released from  
9 their encapsulated particles at the prevailing  
10 wellhead conditions and the formation chemicals are  
11 only released upon reaching the more aggressive  
12 prevailing conditions at the formation.

13

14 **Example 8**

15 Starch was weighed out into a glass container. The  
16 oil well chemical was added while mixing for 5  
17 minutes and then mixed for an additional 5 minutes,  
18 or until uniform using a Powerstat, Variable  
19 Autotransformer set at 80 (3PN168), Bodine Electric  
20 Co, Speed reducer motor (NSE-12R).

21

22 a. Starch used was a 50:50 blend of sago and  
23 tapioca, DD and the oil well chemical used was  
24 Waxtreat 398. The starch:chemical ratio used was  
25 100:40 and the loading was 28.6%.

26 b. Starch used was a high amylose (70%) maize starch  
27 modified by 3% octenyl succinic anhydride and 10%  
28 polyvinyl alcohol and the oil well chemical used  
29 was Waxtreat 398. The starch:chemical ratio used  
30 was 100:80 and the loading was 44.4%.

31 c. Starch used was enzyme converted (alpha amylase)  
32 maltodextrin and the oil well chemical used was

1       Trosquat. The starch:chemical ratio used was  
2       100:38 and the loading was 27.5%.

3       d. Starch used was enzyme converted (alpha amylase)  
4       maltodextrin and the oil well chemical used was  
5       Trosquat. The starch:chemical ratio used was  
6       100:38 and the loading was 27.5%.

7       e. Starch used was a high amylose (70%) maize that  
8       was gelatinised, completely enzymatically de-  
9       branched and retrograded and the oil well  
10      chemical used was Hytreat A560. The  
11      starch:chemical ratio used was 100:24 and the  
12      loading was 19.3%.

13

14      The encapsulated chemicals are mixed as desired and  
15      delivered to production tubing or other well  
16      tubulars through a single fluid line. Once reaching  
17      the target in the well the chemicals are released  
18      through reaction to local conditions.

19

20      The wellhead is the preferred target of the  
21      chemicals delivered in order to protect the tie  
22      backs etc from corrosion or blockage, but it will be  
23      appreciated that the present invention is not in any  
24      way limited to the delivery of chemicals to the  
25      wellhead, and in certain embodiments the delivery  
26      target is another portion of the well, such as the  
27      formation, the reservoir, the casing, production  
28      tubing or other tubular or conduit.

29

30      Typical embodiments of the invention mitigate  
31      compatibility problems with delivery of mixtures of  
32      chemicals to platforms, remote and complex wells

1 through a single injection line. Some embodiments  
2 also facilitate the deployment of certain chemicals  
3 that are difficult to handle, for example, because  
4 they are very corrosive and/or are insoluble in  
5 conventional solvents; for example, polyacrylate wax  
6 inhibitors, either alone or in combination with  
7 other chemicals, where the chemicals or at least one  
8 of them cannot be effectively deployed by  
9 conventional solvents.

10  
11 Certain embodiments also enable the deployment of  
12 oilfield chemicals at high active concentrations,  
13 for example, ethylene vinyl acetate (EVA) wax  
14 inhibitors that cannot be effectively deployed at  
15 >10%v/v by conventional solvents.

16  
17 While starch is a preferred entrapping or coating  
18 medium a range of other materials could be used such  
19 as natural gums, cellulose and derivatives,  
20 polysaccharides, gelatin, wax, fatty acids, acrylic,  
21 carboxyvinyl polymers, polyester, polystyrene,  
22 polycaprolactone, polyvinyl acetate, polyamides,  
23 polyvinyl alcohol, polylactic acid, polyglycolide,  
24 shellac, zein, oil based gels, silica gel and other  
25 materials consisting of mixtures, copolymers,  
26 terpolymers and hydrophobically and/or  
27 hydrophilically modified and cross-linked  
28 derivatives of the above.

29  
30 In certain embodiments the nano/micro particles can  
31 be dispersed in an aqueous or oleic medium depending  
32 upon the encapsulation matrix, and can contain one

- 1 or more soluble or dispersed oilfield production
- 2 chemicals.
- 3
- 4 Modifications and improvements can be incorporated
- 5 without departing from the scope of the invention.

## 1     Claims

2     1.     A method of delivering a chemical to an oil or  
3           gas well, the method comprising associating the  
4           chemical with a carrier, and delivering the  
5           chemical and carrier to the well.

6  
7     2.     A method as claimed in claim 1, wherein the  
8           chemical is encapsulated by the carrier.

9  
10    3.     A method as claimed in any preceding claim,  
11           wherein the chemicals are released from the  
12           carrier upon contact with the produced fluids  
13           in the well.

14  
15    4.     A method as claimed in any preceding claim,  
16           wherein two or more chemicals are delivered via  
17           a single chemical injection conduit.

18  
19    5.     A method as claimed in claim 4, wherein the two  
20           chemicals are mutually incompatible.

21  
22    6.     A method as claimed in claim 4 or claim 5,  
23           wherein the two or more chemicals are released  
24           from the carrier at different locations in the  
25           well.

26  
27    7.     A method as claimed in any preceding claim,  
28           wherein the or each chemical is aggressive,  
29           insoluble or corrosive.

30

1     8.     A method as claimed in any preceding claim,  
2             wherein the chemical and carrier are carried by  
3             a fluid to the desired point of delivery.

4

5     9.     A method as claimed in claim 8, wherein the  
6             fluid phase carries a further chemical to be  
7             delivered to the well.

8

9     10.    A method as claimed in claim 8 or claim 9,  
10            wherein the fluid is aqueous fluid.

11

12    11.    A method as claimed in claim 8, or claim 9  
13            wherein the fluid is oleic or organic fluid.

14

15    12.    A method as claimed in any preceding claim,  
16            wherein the chemical-bearing carrier is  
17            injected at surface.

18

19    13.    A method as claimed in any preceding claim,  
20            wherein the chemical-bearing carrier is  
21            injected at a wellhead.

22

23    14.    A method as claimed in any preceding claim,  
24            wherein the chemical is selected from the group  
25            comprising scale inhibitors, corrosion  
26            inhibitors, wax inhibitors and dispersants,  
27            asphaltene inhibitors and dispersants, hydrate  
28            inhibitors, oxygen scavengers, pour-point  
29            modifiers, hydrogen sulphide scavengers,  
30            demulsifiers, biocides, gel breakers, tracers,  
31            friction reducers, surfactants, de-oilers and  
32            antifoaming agents.



- 1 15. A method as claimed in any preceding claim,  
2 wherein the carrier is associated with the  
3 chemical by a technique selected from the group  
4 comprising coacervation, interfacial  
5 polymerisation, desolvation, extrusion,  
6 agglomeration, emulsion polymerisation,  
7 gelation, chemical vapour deposition, fluid bed  
8 coating, spray drying and combinations thereof.  
9
- 10 16. A method as claimed in any preceding claim,  
11 wherein the carrier is selected from the group  
12 comprising starch or flour, gum arabic, waxes,  
13 PVOH, polylactic acids, dextrans, low viscosity  
14 modified starches, arabinogalactan, gum acacia,  
15 casein, gelatin, carboxymethylcellulose,  
16 tragacanth, karaya, sodium alginate, tannin,  
17 and celluloses.  
18
- 19 17. A method as claimed in any preceding claim,  
20 wherein the chemical is continuously delivered  
21 to the well.  
22
- 23 18. A method as claimed in any preceding claim,  
24 wherein the carrier and chemical forms a  
25 particle.  
26
- 27 19. A method as claimed in claim 18, wherein the  
28 particle size is in the range of 1 $\mu$ m-20 $\mu$ m.  
29
- 30 20. A method as claimed in any preceding claim,  
31 wherein the carrier dissolves into the produced

- 1 fluids from the well after releasing the
- 2 chemical.

## INTERNATIONAL SEARCH REPORT

Intern I Application No  
PCT/GB 01/03547A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 E21B37/06 E21B43/25

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 611 664 A (OSTERHOUDT III M GLENN ET AL) 16 September 1986 (1986-09-16) column 2, line 35 -column 3, line 13; claims 1,2,5-9,12-16 column 4, line 21 - line 49 ----	1-3,13, 14
X	US 4 986 354 A (CANTU LISA A ET AL) 22 January 1991 (1991-01-22)  column 1, line 38 -column 4, line 2 ----- -/--	1-3,8, 10-12, 14,15, 17-20



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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 93 22537 A (PROCTER & GAMBLE) 11 November 1993 (1993-11-11)  page 1, line 1 - line 30 page 4, line 31 -page 5, line 25 page 9, line 35 -page 11, line 15 page 16, line 11 - line 33; claims 1,5,6 -----	1-5,8, 10,11, 14-18,20
X	US 4 986 353 A (CLARK CHARLES R ET AL) 22 January 1991 (1991-01-22)  column 1, line 37 -column 4, line 19 -----	1-3,8, 10-12, 14,15, 17-20

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 01/03547

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4611664	A	16-09-1986	NONE	
US 4986354	A	22-01-1991	NONE	
WO 9322537	A	11-11-1993	US 5922652 A AT 149237 T AU 4227493 A BR 9306321 A CA 2134980 A1 CZ 9402703 A3 DE 69308297 D1 EP 0639240 A1 FI 945196 A HU 70884 A2 JP 7506408 T NO 944206 A NZ 252502 A RU 2111049 C1 SK 132294 A3 WO 9322537 A1	13-07-1999 15-03-1997 29-11-1993 26-03-1996 11-11-1993 14-06-1995 03-04-1997 22-02-1995 04-11-1994 28-11-1995 13-07-1995 04-11-1994 29-01-1997 20-05-1998 11-07-1995 11-11-1993
US 4986353	A	22-01-1991	NONE	

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